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(56) Documents cited
**GB 2228680 A GB 2228679 A GB 2228413 A
GB 2182563 A**

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(54) **Fungicidal wood treatment using hydroxyalkyl phosphines**

(57) Fungicidal hydroxyalkyl phosphine compounds of formula $[\text{HORPR}'_n]_y \text{X}_x$ [wherein R is a divalent C_{1-4} - alkyl group; R' is independently C_{1-4} - alkyl, C_{1-4} - alkenyl or C_{1-4} - hydroxyalkyl; X is an anion such that the compound is soluble; n is 2 or 3; x is 0 or 1 such that $(x + n)$ is 2 or 4; y is equal to the valency of X when x is 1 and y is 1 when x is 0], such as tetrakis (hydroxymethyl) phosphonium salts, are applied to the exposed surfaces of unseasoned or incompletely seasoned timber in order to control sapstain.

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The present invention relates to the treatment of wood, in particular to inhibit discoloration resulting from fungal kattack.

Exposed surfaces of freshly cut timber are susceptible to attack by discoloring fungi in particular blue- stain or sapstain fungi which colour the wood dark and reduce its value or that of articles made from it for use eg in furniture. Hitherto pentachlorophenol has been used to control this problem but its use may give rise to environmental pollution problems.

We have now discovered a composition capable of inhibiting the onset of discoloration but having a significantly reduced influence on the environment.

The present invention provides a method of treating a wood surface susceptible to attack by wood discoloring fungi, which method comprises contacting said surface with a liquid medium comprising a hydroxy alkyl phosphine compound.

There is also provided the use of the hydroxyalkyl phosphine compound for treating wood surfaces susceptible to attack by wood discoloring fungi.

According to our invention hydroxyalkyl phosphine compounds, of the formula $[HORPR'_n]_yX_x$, wherein n is 2 or 3, x is 0 or 1 such that $(n + x) = 2$ or 4; y is equal to the valency of X when x is 1 and is 1 when x is 0; R is a divalent saturated aliphatic hydrocarbyl group of 1-4 carbon atoms; each of R' may be the same or different and represents an alkyl or alkenyl group having up to 4 carbon atoms or a group of the formula HOR-, wherein R is as defined above; and X is an anion such that the phosphorus compound is water soluble are used to control wood discoloring fungi.

In the hydroxyalkyl phosphines, R represents a divalent saturated aliphatic hydrocarbyl group which is an alkylene group of 1-4 carbon

atoms, such as 1,2-ethylene, 1,3-propylene or 1,4-butylene or methylene, which is preferred, or an alkylidene group of 2-4 carbon atoms such as 1,1-ethylidene, 1,1-propylene, 1,1-butylidene or isopropylidene. Each R' may represent an alkyl group of 1-4 carbon atoms, examples of which are methyl, ethyl, propyl and butyl. R' may also represent an alkenyl group of 2-4 carbon atoms, examples of which are vinyl, allyl and methallyl. R' may also represent a group of formula HOR- wherein R is as defined above. Preferably at least one R' group is of formula HOR- and preferably each other R' group is of formula HOR-. Most preferred are those compounds in which three R' groups are hydroxyalkyl, especially hydroxymethyl as in water soluble tetrakis (hydroxymethyl) phosphonium salts (herein after referred to as "THP salts").

The compound tris (hydroxymethyl) phosphine is also effective, but is generally insufficiently stable in marketable formulations to be of commercial interest in itself. However any precursor which yields tris (hydroxy-methyl) phosphine at the wood surface may be used according to our invention.

The preferred tetrakis (hydroxymethyl) phosphonium compounds, on economic grounds, are tetrakis (hydroxymethyl) phosphonium sulphate and the corresponding chloride, bromide and phosphate; however X is present solely as a counter ion and its identity is therefore immaterial. It may be any compatible anion such as nitrate, fluoride, phosphonate, nitrite, sulphite, phosphite, iodide, borate or carbonate or an organic anion such as formate, acetate, benzoate, citrate, tartrate, lactate, propionate, butyrate or a surfactant anion such as an alkyl benzene sulphonate, or alkyl polyalkyleneoxy sulphate. Other phosphonium salts are methyl-, ethyl-, or allyl-tris (hydroxymethyl) phosphonium salts, especially the sulphate or chloride or with X as any other compatible anion such as those listed above.

The wood surface to which the hydroxyalkyl phosphine compound is applied is derived from green freshly felled timber. Thus the surface, which is preferably of sapwood, may be the ends of such timber before debarking, but preferably the surface is of green or unseasoned debarked timber bearing exposed sapwood. This latter timber may be in the form of logs, being the original timber cut laterally or pieces of further diminished size in one or preferably both longitudinal planes. Thus posts, poles, planks, railway sleepers, and blocks may be treated, these items being either in the dimensions for the eventual users, or easily handleable but capable of size reductions by the eventual users, eg blocks of 1-2m length and 0.5-2m other dimensions, for subsequent cutting to form boards of 1-2m length by 0.05- 0.2m wide and 0.01 - 0.1m deep, such as are used for construction of load carrying pallets. The wood surface may also be on wood chips, for subsequent conversion by the user into paper or paper products. Sapstain is primarily a problem of recently felled timber which has not been fully seasoned and of the exposed ends of the timber where it has been cut across the grain. A substantial measure of protection is therefore afforded by applying the fungicide to the exposed ends of the timber without the need to impregnate the timber as a whole. The wood to be treated may be deciduous or coniferous, softwood or hardwood from polar, temperate or equatorial areas. Preferably the wood is softwood and especially coniferous softwood, such as Ponderosa pine, Western Hemlock or Douglas fir; the hardwood Alder is also preferred.

The hydroxyalkyl phosphine may be applied to the wood undiluted but preferably is applied in dilute solution in a solvent which may be organic eg an alcohol or water or mixture thereof. The concentration of hydroxyalkyl phosphine in the solution is usually

0.01- 10% e.g. 0.1-5% or 0.2-3% by weight. The solution is usually at pH 2-12 e.g. 2-10. For convenience of handling the hydroxyalkyl phosphine compound is conveniently transported in the form of an aqueous concentrate containing 5-80% by weight of the phosphine

compound, which concentrate is diluted with water when ready for use. The concentration of active ingredient in the impregnation medium varies according to the absorption capacity of the wood surface and the time of contact of solution and the surface.

Application of the impregnation solution to the wood may be accomplished in a number of ways. It may be applied by painting, spraying dipping or soaking or by use of a variety of vacuum and/or pressure impregnation techniques. The contact usually introduces the hydroxyalkyl phosphine into the wood to a depth of up to 15 mm, usually 5-10 mm. After application the wood is dried or allowed to dry, preferably under conditions minimising distortion.

We have also discovered that if the hydroxy alkyl phosphine is mixed with a quaternary ammonium compound, then there is a synergistic effect and the effectiveness of the combination is significantly greater than with the individual components. The hydroxyalkyl phosphine and quaternary ammonium compound are usually present in weight ratios of 1-99:99-1 eg 10-90:90-10 especially 10-40:90-60 or 90-60:10-40.

The quaternary ammonium compound may for example be an alkylammonium salt having a total of at least 8, usually 10 to 30, e.g. 12 to 24 aliphatic carbon atoms, especially a tri or tetra-alkylammonium salt. Typically alkylammonium compounds for use according to our invention have one or at most two relatively long aliphatic chains per molecule (e.g. chains having an average of 8 to 20 carbon atoms each, usually 12 or 18 carbon atoms) and two or three relatively short chain alkyl groups having 1 to 4 carbon atoms each, e.g. methyl or ethyl groups, preferably methyl groups.

Typical examples include dodecyl trimethyl ammonium salts. Benzalkonium salts having one 8 to 20 C alkyl group, two 1 to 4 carbon alkyl groups and a benzyl group are also useful.

Another class of quaternary ammonium compound useful according to our invention are N-alkyl pyridinium salts wherein the alkyl group has an average of from 8 to 22, preferably 10 to 20 carbon atoms. Other similarly alkylated heterocyclic salts, such as N-alkyl isoquinolinium salts, may also be used.

Another useful class of quaternary ammonium compounds, that are useful are substituted benzyl tri alkyl ammonium salts wherein the benzyl group is substituted by an alkyl chain with 1 to 20, preferably 8 to 15, or most preferably, about 12 carbon atoms and the three alkyl groups contain 1 to 6 carbon atoms and are preferably methyl.

Alkylaryl dialkylammonium salts, having an average of from 10 to 30 aliphatic carbon atoms are useful, e.g. those in which the alkylaryl group is an alkyl benzene group having an average of from 8 to 22, preferably 10 to 20 aliphatic carbon atoms and the other two alkyl groups usually have from 1 to 4 carbon atoms, e.g. methyl groups.

Other classes of quaternary ammonium compounds which are of use in our invention include alkyl imidazoline or quaternised imidazoline salts having at least one alkyl group in the molecule with an average of from 8 to 22 preferably 10 to 20 carbon atoms. Typical examples include alkyl methyl hydroxyethyl imidazolinium salts, alkyl benzyl hydroxyethyl imidazolinium salts, and 2 - alkyl-1-alkylamidoethyl imidazoline salts.

Another class of quaternary ammonium compounds for use according to our invention comprises the quaternized products made from amido amines such as those formed by reacting a fatty acid having 8 to 22 carbon atoms or an ester, glyceride or similar amide forming derivative thereof, with a di or poly amine, such as, for example, ethylene diamine or diethylene triamine, in such a proportion as to leave at least one free amine group.

Typically the quaternary ammonium compound may be any water soluble compound having a positively ionised group comprising a nitrogen atom, and either one or two alkyl groups each having an average of from 8 to 22 carbon atoms.

The anion portion of the quaternary ammonium compound may be any anion which confers water solubility, such as formate, acetate, lactate, tartrate, citrate, chloride, nitrate, sulphate or an alkylsulphate ion having up to 4 carbon atoms such as a methosulphate.

The concentration of quaternary ammonium compound in the impregnation solution is usually 0.01-20% by weight.

This invention is particularly useful for reducing preventing discolouration, and consequent reduction in value of, wood between the time of felling and that of its delivery to the end user, which period is typically 6 to 12 weeks.

This invention is illustrated by the following examples:-

Example 1

Sapwood blocks or coupons 15.0 cm long with a 0.6 cm x 2.54 cm cross section end grain area were cut from freshly-swain Douglas-fir

(Pseudotsuga mensiesii), ponderosa pine (Pinus ponderosa), Western hemlock (Tsuga heterophylla), and red alder (Alnus rubra).

Each coupon was steamed for 10 minutes at 100°C to eliminate any previously established fungi and numbered for later identification. Groups of seven coupons were then individually dipped for 30 seconds in aqueous solutions of tetrakis (hydroxymethyl) phosphonium sulphate (THPS). The solutions contained 5 different concentrations of THPS; coupons were also dipped into water as a control. The

solutions were made by appropriate dilution of the 75% aqueous solution of THPS. After dipping, the coupons were surface dried and each treatment group was placed into a plastic bag. The coupons were then sprayed with a water suspension containing spores and hyphal fragments of Phialophora heteromorpha, Phialophora fastigiata, Ceratocytis picea, Alternaria alternata, Pencillium sp., and Aspergillus niger. The inoculated coupons were incubated at 32° C for 6 weeks.

Following incubation, the coupons were evaluated for the degree of stain on a scale from 0 (no stain) to 10 (completely discoloured). The results below indicate the average degree of stain rating for each group of coupons.

Concentration of THPS	3.2%	1.6%	1.2%	0.8%	0.4%	0% (Control)
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Douglas-fir	0.00	0.00	0.36	0.29	4.14	4.29
Ponderosa pine	3.71	4.43	3.29	7.14	8.14	8.71
Western hemlock	0.00	0.00	0.00	0.00	0.86	4.00
Red alder	0.86	1.29	2.71	0.36	2.00	4.14

Example 2

Further Douglas fir coupons as described in Example 1 were treated in a similar manner to those in Example 1 with solutions comprising:-

- 1 Tetrakis(hydroxymethyl) phosphonium sulphate aqueous solution (as a 75% aqueous solution).
- 2 Higher alkyl benzyl trimethyl ammonium chloride (sold as a 50% aqueous solution under the Trade Mark GLOQUAT C).
- 3 A 1:3 w/w mixture of 1 and 2.
- 4 A 3:1 w/w mixture of 1 and 2.

In each case treatment solution contained 0.2% w/w active ingredients in total.

Results were as follows:-

Solution	Degree of stain rating
1	5.0
2	5.0
3	4.4
4	3.8

CLAIMS

1.

A method for the control of sapstain in unseasoned or incompletely seasoned timber which comprises applying to vulnerable timber surfaces a fungicidal amount of a hydroxyalkyl phosphine compound of the formula $[\text{HORPR}'_n]_y\text{X}_x$ wherein n is 2 or 3, x is 0 or 1 such that $(x+n) = 2$ or 4, y is equal to the valency of X when x is 1 and is 1 when x is 0, R is a divalent alkyl group having up to 4 carbon atoms, each R' , which may be the same or different, is an alkyl or alkenyl group having up to 4 carbon atoms or a hydroxyalkyl group having up to 4 carbon atoms, and X is an anion such that the compound is soluble.

2.

A method according to claim 1 wherein said compound is a tetrakis [hydroxymethyl] phosphonium salt.

3.

A method according to either of claims 1 and 2 wherein said compound is applied in conjunction with a synergistic amount of a water soluble quaternary ammonium salt.

4.

A method according to claim 3 wherein the proportions of said compound to said quaternary ammonium salt is from 1:99 to 99:1 by weight.

5.

Timber at least the exposed ends of which have been impregnated with a hydroxyalkyl phosphate compound as aforesaid.

Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

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Relevant Technical fields

(i) UK CI (Edition K) A5E (EAB, EBB)

(ii) Int CI (Edition 5) A01N 57/20

Databases (see over)

(i) UK Patent Office

(ii) Online Databases: CAS Online

Search Examiner

S J Quick

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10 May 1991

Documents considered relevant following a search in respect of claims

1-5

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2228680 A (ALBRIGHT & WILSON) especially pages 12 (3rd paragraph) and 13 (1st paragraph)	1 at least
X	GB 2228679 A (ALBRIGHT & WILSON) especially page 12, (1st and 2nd complete paragraph)	1 at least
X	GB 2228413 A (ALBRIGHT & WILSON) especially pages 13 (3rd complete paragraph) and 14 (1st complete paragraph)	1 at least
X	GB 2182563 A (ALBRIGHT & WILSON) especially page 1, lines 89-95 and 113-118	1 at least

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Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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